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METHOD FOR PRODUCING POLYPROPYLENE UNDER HIGH PRESSURE

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A method for producing homopolymers of propylene or copolymers of propylene with other olefins or their mixtures, where polymerization is carried out at pressures from 100 to 3000 bar and at temperatures from 100 to 330°C and a metallocene catalyst system is used as catalyst.

Description

This invention concerns a method for producing homopolymers of propylene or copolymers of propylene with other olefins or their mixtures.

Methods for producing homo- and/or copolymers of propylene at low pressures using Ziegler catalyst systems are known, for example, from EP-A 3 51 392 and EP-A 3 21 852. However, in this case we have heterogeneous systems, the productivities are unsatisfactory, and the choice of monomers is limited.

The task of this invention therefore was to make available a method for producing homo- and/or copolymers of propylene that does not have these disadvantages.

Accordingly, a method [for production] of homopolymers of propylene or copolymers of propylene with other olefins or their mixtures was found, in which polymerization is carried out at pressures from 100 to 3000 bar and at temperatures from 100 to 330°C and a metallocene catalyst system is used as catalyst.

According to these methods [sic] one obtains linear homopolymers of propylene or linear copolymers that have short chain branchings.

Cyclic olefins with 3-12 C atoms, preferably with 4-8 C atoms, dienes, especially α,ω -dienes with 4-10 C atoms like 1,5-hexadiene, and olefins with 2-10 C atoms, preferably ethylene, butenes and hexenes, have proven to be suitable as olefins that can be copolymerized with propylene, where the α -olefins are especially preferred. These olefins can also have aryl or heteroelement substituents like styrene or unsaturated substituted silanes.

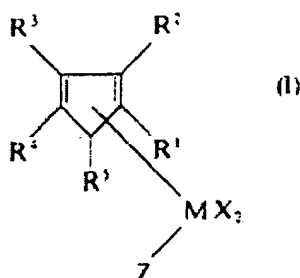
As a rule, these comonomers are used in amounts from 0.1-99.9 wt%, preferably in amounts from 1-99 wt%, with respect to the amount of propylene.

Metallocene catalyst systems that contain as active component, among other things, a complex compound of metals of the IV and V side groups of the periodic system, especially titanium, zirconium, hafnium, vanadium, niobium or tantalum, are used as catalysts. Complex compounds in which the metal atom is bonded to unsaturated cyclic hydrocarbon atoms via π bonds, for example, cyclopentadienyl, fluorenyl or indenyl groups, are preferably used. In

addition, the preferably used complex compounds are characterized by the fact that the metal atom can be linked to still other ligands, especially fluorine, chlorine, bromine or iodine or a C₁-C₁₀ alkyl, for example, a methyl, ethyl, propyl or butyl group. Especially suitable complex compounds here contain chlorine in particular.

Preferred metallocene catalyst systems contain, as active components

a) a metallocene complex of general formula I



in which the substituents have the following meanings:

M represents titanium, zirconium, hafnium, vanadium, niobium or tantalum,

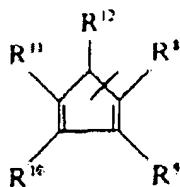
X represents fluorine, chlorine, bromine, iodine, hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl or -OR⁶, where

R⁶ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl in each case with 1-10 C atoms in the alkyl residue and 6-20 C atoms in the aryl residue,

R¹-R⁵ represent hydrogen, C₁-C₁₀ alkyl, 5- to 7-member cycloalkyl, which in turn can have a C₁-C₆ alkyl as substituent, C₆-C₁₅ aryl or arylalkyl, where optionally two adjacent residues together can stand for unsaturated cyclic groups having 4-15 C atoms, or Si(R⁷)₃, and

R⁷ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl or C₃-C₁₀ cycloalkyl,

Z stands for X or



where the residues

R⁸-R¹² represent hydrogen, C₁-C₁₀ alkyl, 5- to 7-member cycloalkyl, which in turn can have a C₁-C₁₀ alkyl as substituent, C₆-C₁₅ aryl or arylalkyl, where optionally two adjacent residues together can stand for cyclic groups having 4-15 C atoms, or

Si(R¹³)₃, and

R¹³ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl or C₃-C₁₀ cycloalkyl, or where the residues

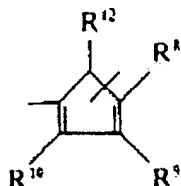
R⁴ and Z together form a group -[Y(R¹⁴)₂]_n-E-, in which

Y stands for silicon, germanium, tin or carbon,

R^{14} stands for C_1 - C_{10} alkyl, C_3 - C_{10} cycloalkyl or C_6 - C_{10} aryl,

n stands for the numbers 1, 2, 3 or 4,

E stands for



or A, where

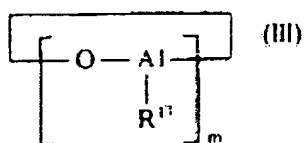
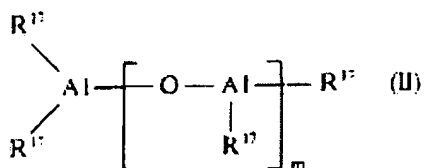
A means $-O-$, $-S-$, $>NR^{15}$ or $>PR^{15}$,

R^{15} represents C_1 - C_{10} alkyl, C_6 - C_{15} aryl, C_3 - C_{10} cycloalkyl, alkylaryl or $Si(R^{16})_3$

and R^{16} represents C_1 - C_{10} alkyl, C_6 - C_{15} aryl, C_3 - C_{10} cycloalkyl or alkylaryl,

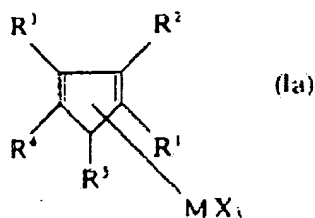
and

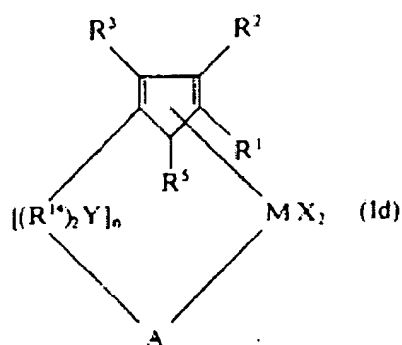
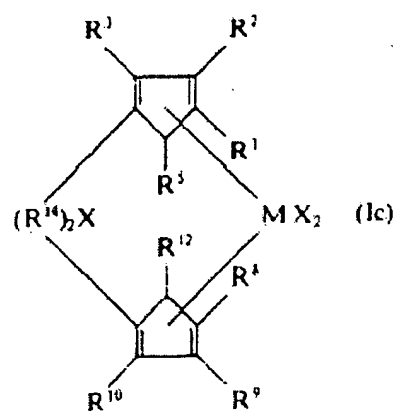
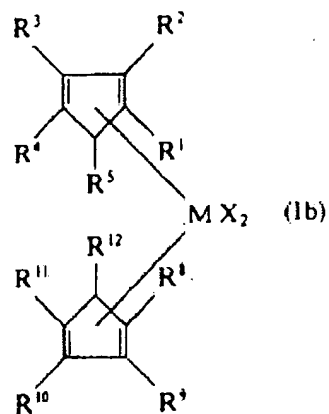
b) an open chain or cyclic alumoxane compound of the general formula II or III



where R^{17} represents a C_1 - C_4 alkyl group and m stands for a whole number from 5 to 30.

Of the metallocene complexes of general formula I,





and

are preferred.

Of the compounds of formula Ia, those in which M represents titanium, zirconium or hafnium, X represents chlorine and R^1 - R^5 represent hydrogen or C_1 - C_4 alkyl, are especially preferred.

Of the compounds of formula Ib, those in which M stands for zirconium or hafnium, X stands for chlorine,

R^1 - R^5 represent hydrogen, C_1 - C_4 alkyl or $Si(R^7)_3$,
 R^6 - R^{10} represents hydrogen, C_1 - C_4 alkyl or $Si(R^{13})_3$
 are especially preferred.

The compounds of formula Ib in which the cyclopentadienyl residues are the same, preferably the unsubstituted cyclopentadienyl residues, are especially suitable.

Of the compounds of formula Ic those in which
 R^1 and R^8 are the same and stand for hydrogen or C_1 - C_{10} alkyl groups
 R^5 and R^{12} are the same and stand for hydrogen, methyl, ethyl, isopropyl or tert-butyl groups,

R^2 , R^3 , R^9 and R^{10} : R^3 and R^{10} have the meaning C_1 - C_4 alkyl and R^2 and R^9 have the meaning hydrogen*, or two adjacent residues R^2 and R^3 and R^9 and R^{10} together stand for unsaturated cyclic groups having 4-12 C atoms,

R^{14} stands for C_1 - C_8 alkyl,

M stands for zirconium or hafnium,

Y stands for silicon, germanium, tin or carbon and

X stands for chlorine.

Examples of especially suitable complex compounds are, among others
 dimethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride,
 diethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride,
 methyl ethyl silanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(-3-tert-butyl-5-ethylcyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)-dimethylzirconium,
 dimethylsilanediylbis(-2-methylindenyl)zirconium dichloride,
 diethylsilanediylbis(-2-methylindenyl)zirconium dichloride,
 dimethylsilanediylbis(-2-ethylindenyl)zirconium dichloride,
 dimethylsilanediylbis(-2-isopropylindenyl)zirconium dichloride,
 dimethylsilanediylbis(-2-tert-butylindenyl)zirconium dichloride,
 diethylsilanediylbis(-2-methylindenyl)zirconium dichloride,
 dimethylsilanediylbis(-2-methylindenyl)zirconium dichloride,
 dimethylsilanediylbis(-2-methyl-5-methylcyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(-2-methyl-5-ethylcyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(-2-ethyl-5-isopropylcyclopentadienyl)zirconium dichloride,
 dimethylsilanediylbis(-2-methylindenyl)zirconium dichloride,

* [Translator's note: This original wording " R^2 , R^3 , R^9 and R^{10} : R^3 and R^{10} have the meaning C_1 - C_4 alkyl and R^2 and R^9 have the meaning hydrogen" does not make grammatical sense; this is my guess at what was meant.]

dimethylsilanediybis(-2-methylbenzindenyl)zirconium dichloride and dimethylsilanediybis(-2-methylindenyl)hafnium dichloride.

Among the compounds of general formula Id those in which

M stands for zirconium or hafnium,

X stands for chlorine or C₁-C₁₀ alkyl,

Y stands for silicon or carbon if n = 1 or for carbon if n = 2,

R¹⁴ stands for C₁-C₈ alkyl, C₅ and C₆ cycloalkyl or C₆-C₁₀ aryl,

A stands for -O-, -S-, >NR¹⁵ and

R¹-R³ and R⁵ stand for hydrogen, C₁-C₁₀ alkyl, C₃-C₁₀ cycloalkyl, C₆-C₁₅ aryl or Si(R⁷)₃.

The synthesis of such complex compounds can take place by substantially known methods, where the conversion of the correspondingly substituted cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum is preferred.

Examples of the corresponding preparation processes are described, among other places, in Journal of Organometallic Chemistry, 369 (1989), 359-370.

The metallocene complexes can also be in cationic form, as described in EP-A 2 77 003 and EP-A 2 77 004.

Besides the complex compound, the metallocene catalyst systems as a rule also contain oligomer alumoxane compounds of general formula II or III, where R¹⁷ preferably stands for methyl or ethyl groups and m preferably stands for a number from 10 to 25.

The preparation of these oligomer alumoxane compounds usually takes place by the reaction of a solution of a trialkylaluminum with water and is described, among other places, in EP-A 2 84 708 and US-A 47 94 096.

As a rule, the oligomer alumoxane compounds that are obtained are in the form of a mixture of both linear and cyclic chain molecules of various lengths, so that m is to be seen as an average value. The alumoxane compounds can also be in the form of a mixture with other metal alkyls, preferably with aluminum alkyls.

With the method in accordance with the invention it turned out to be advantageous to use the complex compound of metals of the IV and V side groups of the periodic system and the oligomer alumoxane compound in amounts such that the atomic ratio between aluminum from the oligomer alumoxane compound and the transition metal from the complex compound of metals of the IV and V side group of the periodic system lies in the range from 10:1 to 10⁶:1, especially in the range from 10:1 to 10⁴:1.

For the method in accordance with the invention the catalysts are preferably used in an amount from 10⁻¹ to 10⁻⁹, preferably 10⁻² to 10⁻⁵ mol of metal per liter.

The method can be carried out in the conventional reactors that are used for high pressure polymerization, for example, stirred autoclaves.

It turned out to be advantageous first to mix the complex compound of metals of the IV and V side group of the periodic system with oligomer alumoxane compound before the polymerization, so that an activated catalyst system forms. The length of this activation step is usually 1-120 min, preferably 10-100 min. The mixing is preferably carried out so that the complex compound is brought into contact with the solution of the oligomer alumoxane compound in an inert solvent, for example, benzene, toluene, hexane, heptane or their mixtures, at temperatures from 0 to 50°C.

The method in accordance with the invention can be conducted so that the solutions of complex compounds and oligomer alumoxane compounds are mixed before the reactor and/or are fed into the reactor at several sites. The polymerization can be carried out batchwise or continuously. The polymerization is carried out at pressures from 100 to 3500 bar, preferably from 500 to 3000 bar, especially from 1000 to 3000 bar, and at temperatures from 100 to 330°C, preferably from 120 to 300°C, especially from 120 to 250°C. The residence times lie in the range from 20-240, preferably 30-120 sec.

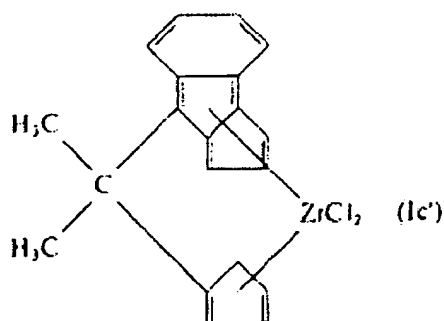
The important advantages of the method in accordance with the invention lie in the fact that high productivities are achieved, the choice of comonomers is very large, and high conversions are achieved at short residence times and high molecular weights are achieved.

Examples

Example 1

Preparation of a propylene homopolymer (PP)

440 mg (\approx 1 mmol)



was dissolved in a mixture of 50 mL (36 g, 0.5 mol) aluminum trimethyl and 290 g 1.53 mol toluene solution of methyl aluminoxane (0.5 mol) in 10 L toluene. 10 m³ propylene/h and the above-described solution were dispensed to a continuously operating high-pressure stirred autoclave under exclusion of air and moisture.

The test conditions and results are given in Table 1.

The average molecular weight \overline{M}_w (weight average) was determined by gel permeation chromatography.

Table 1

① Temperatur [°C]	② Druck [bar]	g lc'/h	③ Verweilzeit [min]	④ Produktivität [g PP/g lc' · h]	\overline{M}_w
149	1510	0.17	1.5	8380	2000

Key: 1 Temperature
2 Pressure
3 Residence time
4 Productivity

Example 2

Preparation of a propylene-ethylene copolymer

The procedure was carried out as in Example 1, but a mixture of propylene and ethylene was polymerized.

The test conditions and results are summarized in Table 2.

Table 2

① Temperatur [°C]	② Druck [bar]	g lc'/h	③ Gew.-% Propylen zu Gew.-% Ethylen im Gasgemisch	④ Produktivität [g Polymer/g lc' · h]	\overline{M}_w
190	1508	0.078	77/23	24 358	10 000

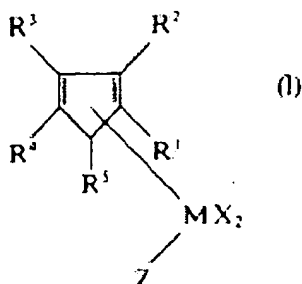
Key: 1 Temperature
2 Pressure
3 wt% propylene to wt% ethylene in the gas mixture
4 Productivity

Claims

1. A method for producing homopolymers of propylene or copolymers of propylene with other olefins or their mixtures, which is characterized by the fact that the polymerization is carried out at pressures from 100 to 3000 bar and at temperatures from 100 to 330°C and a metallocene catalyst system is used as catalyst.

2. A method as in Claim 1, which is characterized by the fact that one uses a metallocene catalyst system that contains, as active components,

a) a metallocene complex of general formula I



in which the substituents have the following meanings:

M represents titanium, zirconium, hafnium, vanadium, niobium or tantalum,

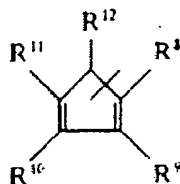
X represents fluorine, chlorine, bromine, iodine, hydrogen, C₁-C₁₀ alkyl, C₆-C₁₅ aryl or -OR⁶, where

R⁶ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl in each case with 1-10 C atoms in the alkyl residue and 6-20 C atoms in the aryl residue,

R¹-R⁵ represent hydrogen, C₁-C₁₀ alkyl, 5- to 7-member cycloalkyl, which in turn can have a C₁-C₆ alkyl as substituent, C₆-C₁₅ aryl or arylalkyl, where optionally two adjacent residues together can stand for unsaturated cyclic groups having 4-15 C atoms, or Si(R⁷)₃, and

R⁷ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl or C₃-C₁₀ cycloalkyl,

Z stands for X or



where the residues

R⁸-R¹² represent hydrogen, C₁-C₁₀ alkyl, 5- to 7-member cycloalkyl, which in turn can have a C₁-C₁₀ alkyl as substituent, C₆-C₁₅ aryl or arylalkyl, where optionally two adjacent residues together can stand for cyclic groups having 4-15 C atoms, or

Si(R¹³)₃, and

R¹³ represents C₁-C₁₀ alkyl, C₆-C₁₅ aryl or C₃-C₁₀ cycloalkyl, or where the residues

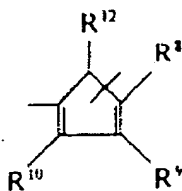
R⁴ and Z together form a group -[Y(R¹⁴)₂]_n-E-, in which

Y stands for silicon, germanium, tin or carbon,

R¹⁴ stands for C₁-C₁₀ alkyl, C₃-C₁₀ cycloalkyl or C₆-C₁₀ aryl,

n stands for the numbers 1, 2, 3 or 4,

E stands for



or A, where

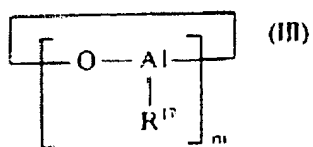
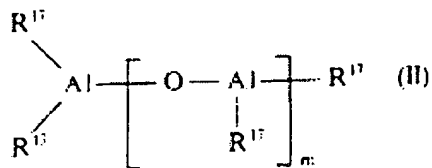
A means $-O-$, $-S-$, $>NR^{15}$ or $>PR^{15}$,

R^{15} represents C_1-C_{10} alkyl, C_6-C_{15} aryl, C_3-C_{10} cycloalkyl, alkylaryl or $Si(R^{16})_3$

and R^{16} represents C_1-C_{10} alkyl, C_6-C_{15} aryl, C_3-C_{10} cycloalkyl or alkylaryl,

and

b) an open chain or cyclic alumoxane compound of the general formula II or III



where R^{17} represents a C_1-C_4 alkyl group and m stands for a whole number from 5 to 30.